MULTIFUNCTIONAL DENDRIMER-LIKE AND SEQUENCE-DEFINED POLYMERIC SYSTEMS USING THIOLACTONE CHEMISTRY

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ABSTRACT

Thiol-ene chemistry is a metal-free, click-like, versatile tool which provides highly-efficient, oxygen and water tolerant reactions. However, the usage of thiols has some drawbacks due to unpleasant smell and low shelf-life stability. To overcome these problems, our group developed an approach based upon thiolactones as thiol precursors for polymer synthesis, which then allowed for site-specific post polymerization modification (PPM) and sequence-control approaches. This method allowed the one-pot, atom-efficient, nucleophilic ring-opening of a thiolactone unit by a primary amine and consequent formation of a reactive thiol moiety which could then undergo a thiol-ene click reaction in situ. This concept not only permits the stability of thiols, but also promotes the introduction of new functionalities [1-3].

In the first part of the present study, multifunctional architectures were targeted via PPM of a star PEG using a thiolactone derivative. Functional groups were introduced onto the PEG structures through the aminolysis of the thiolactone ring and consequent thiol-ene addition (Figure 1a).

In a second part of the project, a thiolactone based, protecting group free, solid phase, two-step iterative protocol was used for the preparation of sequence-defined oligomers (Figure 1b). The comparison of manual and automated syntheses of those oligomers (up to decamers) will be presented along with their scalability from proof of concept to material for potential applications, highlighting the importance of sequence-controlled chemistry.

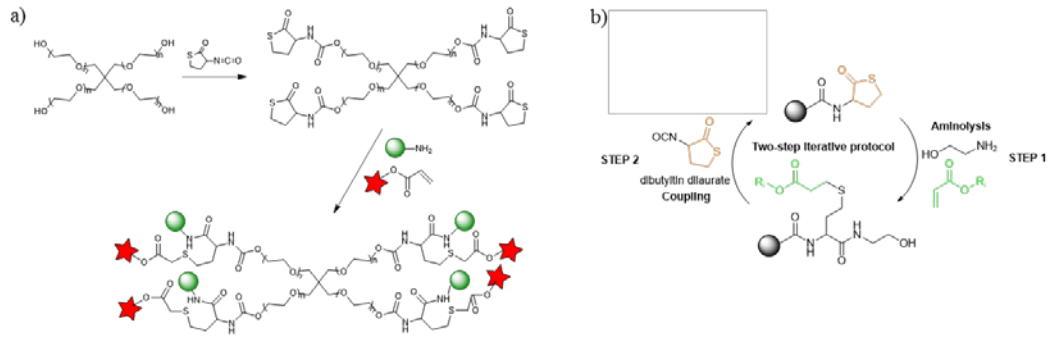

Fig. 1: a) General strategy used for preparing multifunctional macromolecular architectures b) Two-step, iterative protocol for the synthesis of sequence-defined oligomers ort legend to figure

References

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